International Journal of Sciences:
Basic and Applied Research
(IJSBAR)

ISSN 2307-4531
(Print & Online)

http://gssrr.org/index.php?journal=JournalOfBasicAndApplied

Cooxidation of Chalcones and Oxalic acid using Chromium (VI)

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Abstract

Chalcones can be easily oxidized in presence of oxalic acid, by Cr(VI) in acetic acid medium, the rate of cooxidation was found to be a fractional order with respect to the chalcones and its substituents. The order with respect to the chromic acid is unity whereas order with respect to oxalic acid is also a fractional order. The effect of various parameters such as $[H^+]$, [NaCl], $[NaNO_3]$ and dielectric constant of the medium by changing the (v/v) ratio of acetic acid and water content were studied .The intermediate is formed between chalcones and a chromic acid – oxalic acid complex, the presence of the molecule of oxalic acid within the complex facilitates the direct three electron – reduction of Cr (VI) to Cr (III), which is the rate – limiting step. From kinetic data obtained the activation parameters have been computed and suitable mechanism is proposed.

Keywords: Chalcones; cooxidation; chromic acid; oxalic acid

1. Introduction

Chromic acid [Cr(VI)] is an important and useful tool in the hands of chemists both for preparative and analytical purposes .For over a century [Cr(VI)] has been used as an effective oxidizing agent to oxidize almost all organic compounds and some inorganic compound [1]. To site for a few examples, Westheimer and coworkers have reported many features in the mechanistic study of the oxidation of many alcohols by [Cr(VI)], and they concluded that chromic acid oxidizes alcohols via a rapid reversible formation of a

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chromate ester which undergoes a rate determining decomposition by cleavage at the α–carbon hydrogen bond, Rocek and Hasan [2], Venkatasubramanian and coworkers have observed that the chromic acid oxidation of a mixture of oxalic acid and isopropyl alcohol proceeds much faster than the oxidation of either of the two substrates alone. They observed a very remarkable observation that the alcohols undergo a two - electron oxidation and oxalic acid a one - electron oxidation and some other studies have been used [Cr(VI)] as an oxidant [3-7].

Literature survey reveals that there is less kinetic and mechanistic studies involving chalcones or phenyl styryl ketones were done. The utility of chalcones due to their usefulness as in synthesis of various heterocyclic compounds, as plant origin [8] and exhibit antimalarial [9], antibacterial [10], antifibrogenic [11], anticancer [12], antitrichomonal [13], antinflammatory [14], antileishmanial [15], cytotoxic and anti-Trypanosoma cruzi [16] activities. Chalcones or phenyl styryl ketones are of great interest because they have a unique structural feature of having a >C =O functional group in conjugation with >C = C< and the whole molecule is in conjugation, hence in the present investigations the kinetic and mechanistic study of the oxidation of several chalcones and oxalic acid were studied in aqueous acetic acid medium. Chalcones are oxidized by different oxidizing agents and in all these reactions either >C = C< or >C= O< is attacked by various oxidants that have been used for oxidation of chalcones [17-23] in the present study the cooxidation of chalcones and oxalic acid in aqueous acetic acid medium was made to find the rate of reaction and the effect of substituents on the rate of oxidation.

2. Experimetal

2.1. Materials

Benzaldehyde and acetophenone were LR grade and were used after distillation as described in literature [24]. Substituted benzaldehydes, substituted acetophenone were AR grade. Chalcones were prepared by the standard procedure [25], recrystallized as described in the literature and their purities were checked by usual methods by comparing the melting points of chalcones with values given in the literature[26]. Conductivity water was used throughout the course of the investigation. Acetic acid (AR) was twice distilled over chromic oxide containing acetic anhydride [31] (bp 118˚C).

2.2. Kinetic Measurements

Solutions of chalcones and chromic acid prepared in aqueous acetic acid medium and oxalic acid prepared in water were thermally equilibrated for 2 h before each run. The reactions were carried out under pseudo - first order conditions by keeping an excess of [chalcones] and [oxalic acid] over [oxidant], maintaining the ionic strength constant (0.2M) by adding sodium nitrate.The kinetics of the reactions were studied in acetic acid medium 50% (v/v) in the blackened flasks to avoid any photochemical decomposition and the kinetics of the reactions were followed by monitoring the reduction of Cr(VI) iodometrically at regular intervals of time. Under this conditions of the experiments the solvent were not oxidized. Rate constant were computed from the linear (r>0.99) plot of log [Oxidant] against time .In the evaluation of rate coefficients, the kinetics were followed to nearly 75% reaction. Duplicate kinetics run showed that the rates were reproducible with 3 %. The second order rate constant k_2 was obtained from the relation $k_2 = k_1 / [\text{chalcones}]$ where k_1 is the pseudo-first order rate constant.

2.3. Product analysis

The product analysis was carried out under kinetic conditions. Under the specified conditions of cooxidation of chalcones and oxalic acid in aqueous acetic acid medium. It was observed that phenyl acetaldehyde and benzoic acid were detected by TLC and compared with those of authentic samples. In the case of substituted chalcones containing substituents in the aldehydes moiety the product was corresponding substituted benzoic acid and phenyl acetaldehyde.

3. Results and Discussion

The oxidation of chalcones, substituted chalcones by Cr(VI) in presence of oxalic acid in aqueous acetic acid medium was carried out at 308 K showed the following features:

- The order with respect to the [Cr(VI)] under the condition [chalcones] >> [Cr(VI)], the order in [Cr(VI)] is unity as revealed by the linear plots of log [Cr(VI)] against time (Table 1).
- The order with respect to chalcones follows fractional order in [unsubstituted chalcones] and [substituted chalcones] as revealed by the slopes of the plots of log k_1 against log [substrates]. (Table 1: Fig 1).

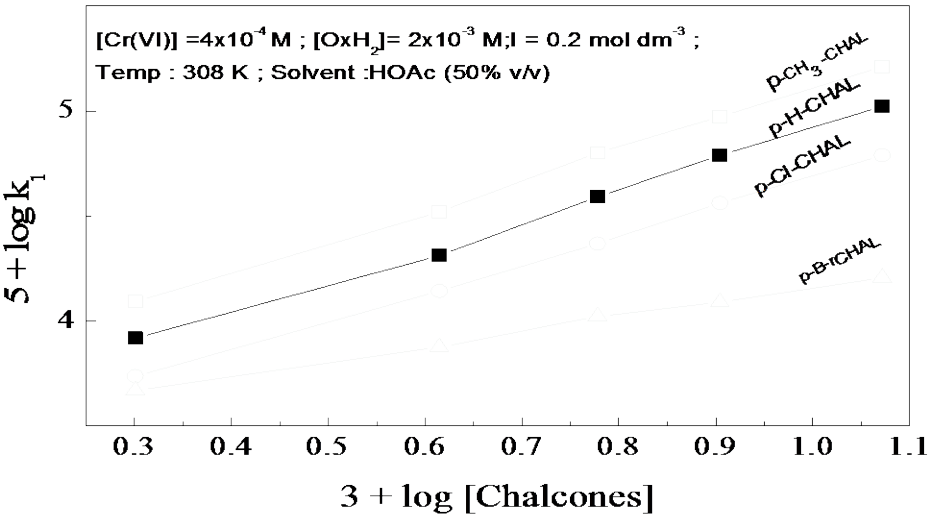


Fig.1 Plots of log k_1 against log [substrates]

Table 1: Effects of varying [reactants] on the reaction rate :

I = 0.2 mol dm^{-3} ; Temp : 308 K ; Solvent :HOAc (50% v/v)

10^3 [CHAL] Mol dm^{-3}	10^4 [Cr(VI)] Mol dm^{-3}	10^3 [OxH_2] Mol dm^{-3}	10^4 k_1 (S^{-1})			
			H-CHAL	**CH_3- CHAL**	**Cl- CHAL**	**Br- CHAL**
2	4	2	0.08245	0.1234	0.05435	0.04658
4	4	2	0.20474	0.33097	0.13847	0.07473
6	4	2	0.39012	0.63183	0.23356	0.10494
8	4	2	0.61532	0.94016	0.36442	0.12226
10	4	2	1.05224	1.62414	0.61372	0.16042
		r	0.99	0.98	0.99	0.99
		slope	1.45	1.46	1.37	0.71
2	2	2	0.04282	0.1134	0.03435	0.03581
2	4	2	0.08245	0.1424	0.06724	0.09445
2	6	2	0.1845	0.2144	0.12824	0.10245
2	8	2	0.2436	0.3211	0.2458	0.16824
2	10	2	0.3210	0.4234	1.2020	0.19846
2	4	2	0.08245	0.09343	0.05210	0.04209
2	4	4	0.20125	0.35025	0.10445	0.06239
2	4	6	0.4321	0.73218	0.16289	0.08279
2	4	8	0.7188	1.19812	0.21889	0.09952
2	4	10	1.04956	1.69821	0.26117	0.11998
		r	0.98	0.99	0.99	0.99
		slope	1.76	1.81	1.01	0.64

- The o*rder with respect to oxalic acid* follows fractional order in oxalic acid as revealed by the slopes of the plots of log k_1 against log [oxalic acid]. (Table 1 Fig 2).

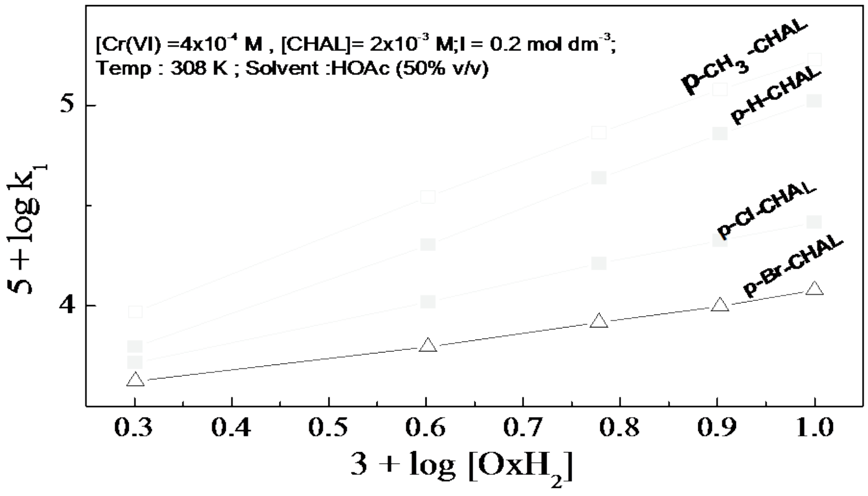
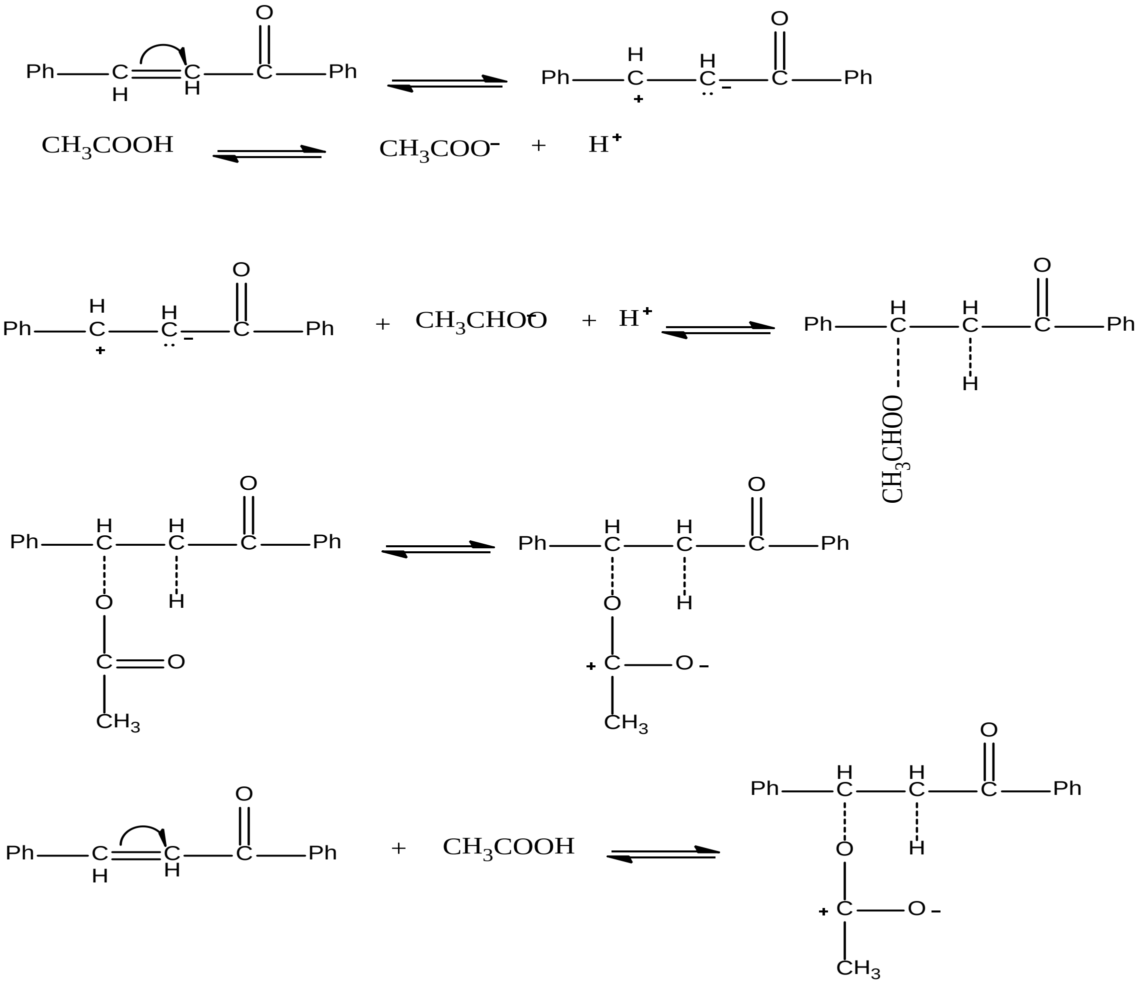


Fig.2, Plots of log k_1 against log [oxalic acid]



Scheme-I

A thought provoking results were obtained, when the cooxidation reactions were carried out at different concentrations of acetic acid, in acetic acid -water mixture. We witness that virtually there is no change in the rate of cooxidation. The rate of cooxidation of chalcones by Cr(VI) in presence of oxalic acid remain constant, though acetic acid proportion is increased in acetic acid-water mixture. Therefore in all probability it can be rightly assumed that the following equilibrium exists between chalcones and aqueous acetic acid **Scheme -I.**

According to scheme-I, the Chromic acid - Oxalic acid complex (C_l) is coordinated to chalcones - acetic acid complex forming an activated complex (C_2) which then undergo concerted intramolecular electronic rearrangement to yield the products in one step.

$$(COOH)_2 + Cr(VI) \overset{k_1}{\rightleftharpoons} C_1 \qquad (1)$$

$$C_1 + CHAL \overset{k_2}{\rightleftharpoons} \text{products} \qquad (2)$$

The concentration is given by equation (3)

$$[C_1] = \frac{k_1\,[(COOH\,)_2\,][Cr\,(VI)]_{Tot}}{1+k_1\,[(COOH\,)_2\,]} \qquad (3)$$

where

$$[Cr(VI)]_{Tot} = [Cr(VI)] + [C_1]$$

Since

$$V = k[C_1] + [CHAL]$$

$$V = k_{exp}\,[Cr(VI)] \qquad (4)$$

$$[CHAL]/k_{exp} = 1/k + 1/k[(COOH_2)] \qquad (5)$$

The validity of the above equation can be tested by plotting $[CHAL]/k_{exp}$ verses $[(COOH)_2]$ very good slope line is obtained which support the assumption of the complex formation. The oxidation of this complex can be regarded as two independent reactions and the rate law can be written as:

$$\frac{-d[Cr\,(VI)]}{dt} = k_1[CHAL][Ox_2H_2][Cr(VI)] + k_2[OxH_2]^2[Cr(VI)]$$

$$= k_{obs}\,[Cr(VI)]$$

$$k_{obs} = k_1[CHAL][OxH_2] + k_2[OxH_2]^{1.76} \qquad (6)$$

As the oxidation is increases with increase of oxalic acid conc. At low conc. The second term of (6)

$k_{obs} = k_1[CHAL][OxH_2]$ can be neglected.

$$\frac{-dk_{obs}}{[CHAL]} = k_1[Ox_2H_2] \qquad (7)$$

The above equation is a linear equation

If we consider the scheme

$$OxH_2 + H_2CrO_4 \xrightleftharpoons{k_1} C_1$$

$$C_1 + CHAL \xrightleftharpoons{k_2} C_2$$

$$C_2 \xrightleftharpoons{k_3} \text{product}$$

$$\text{Rate} = k_3[C_2] = k_{obs}\ [Cr(VI)]$$

$$C_1 = k_1[OxH_2][H_2CrO_4]$$

$$C_2 = k_2[C_1][CHAL]$$

$$[Cr(VI)]_{Tot} = [H_2CrO_4] + k_1[OxH_2][H_2CrO_4] + k_2k_1[OxH_2][H_2CrO_4][CHAL]$$

Rearranging:

$$[Cr(VI)]_{Tot} = [H_2CrO_4] + k_1[OxH_2][H_2CrO_4] + k_2k_1[OxH_2][H_2CrO_4][CHAL]$$

$$k_3[C_2] = k_{obs}\ [H_2CrO_4]\{1 + k_1[OxH_2] + k_2k_1[OxH_2][CHAL]\}$$

$$= k_3k_2k_1[OxH_2][H_2CrO_4][CHAL]$$

$$\frac{[OxH_2]}{k_{obs}} = \left[\frac{1}{k_3k_2k_1} + \frac{[OxH_2]}{k_2k_1}\right]\left[\frac{1}{[CHAL]} + \frac{[OxH_2]}{k_3}\right]$$

The above equation is similar to equation obtained by Venkatasubramanian and coworkers The rate of cooxidation increases with an increase of $[H^+]$ and the log-log plot of initial rate against $[H^+]$ gave a straight line ,from the slope the order with respect to $[H^+]$ is a fractional.

The rate of oxidation of chalcones remains constant when the ionic strength of the medium is increased. Effect of adding sodium chloride also studied and there is no change in the rates of oxidation of chalcones by the addition of sodium chloride. And addition of aluminium nitrate suppresses the oxidation of chalcones with Cr(VI) in presence of oxalic acid.

Table -2: Effects of adding Aluminum nitrate on the reaction rate :

[CHAL] = 2.0 x 10 $^{-3}$ mol dm $^{-3}$; [Cr(VI)] = 4.0 x10 $^{-4}$ mol dm^{-3} ; [OxH2] = 2.0 x 10 $^{-3}$ mol dm^{-3} ;

I = 0.2 mol dm^{-3} ; Temp : 308 K ; Solvent : HOAc (50% v/v)

[Aluminum nitrate]M	10 ^{4}k$_1$(S^{-1})
0.00	0.082452
1.00	0.04286
1.50	0.01234
2.00	0.00680
2.50	0.00242

The rate of cooxidation was measured at different temperatures (308-323 K) for both the unsubstituted chalcones (CHAL) and the substituents on benzaldehyde and acetophenone at para position (X-CHAL & CHAL-X), and the Arrhenius plot of log k_2 versus 1/T was all linear (Table 3.Figure 3,4).

(Table -3: Arrehinus Plot) Activation parameters at para position of Benzaldehyde and Acetophenone Sides :

[CHAL] = 2.0 x 10 $^{-3}$ mol dm $^{-3}$; [Cr(VI)] = 4.0 x10 $^{-4}$ mol dm^{-3}

[OxH$_2$] = 2.0 x 10 $^{-3}$ mol dm^{-3} ; I = 0.2 mol dm^{-3} ; Solvent : HOAc (50% v/v)

Substrate	10 ^{4} k$_1$ (S^{-1})			
	308	313	318	323
CHAL	0.08245	0.15179	0.30424	0.55654
p-CH$_3$- CHAL	0.12340	0.22991	0.43616	0.77021
p-Cl- CHAL	0.05435	0.10345	0.20584	0.36952
p-Br- CHAL	0.04658	0.083199	0.15225	0.30277

p-NO_2-CHAL	0.000218	0.000467	0.000916	0.001977
CHAL-pCH_3	0.539514	0.86297	1.73782	3.23592
CHAL-pCl	0.120226	0.23988	0.41304	0.83176
CHAL-pBr	0.042652	0.057801	0.10964	0.26302
CHAL-pNO_2	0.0011967	0.0019054	0.0038019	0.008317

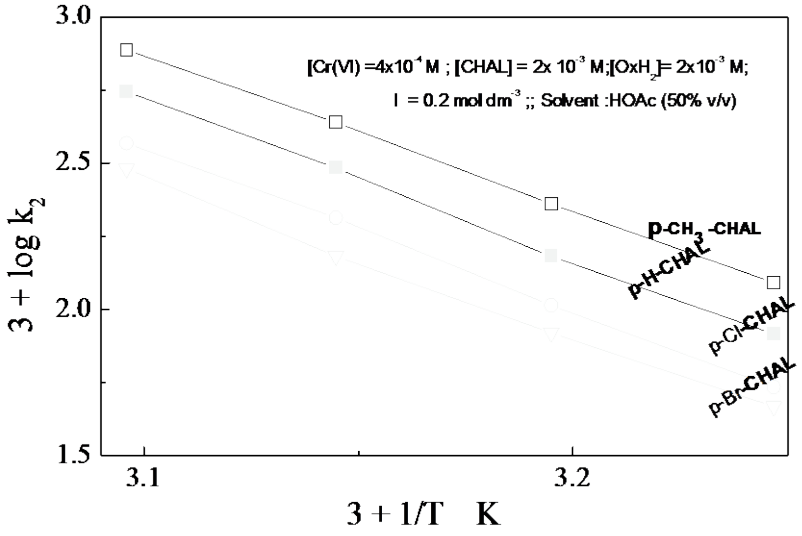


Fig.3: plot of log k_2 versus 1/T

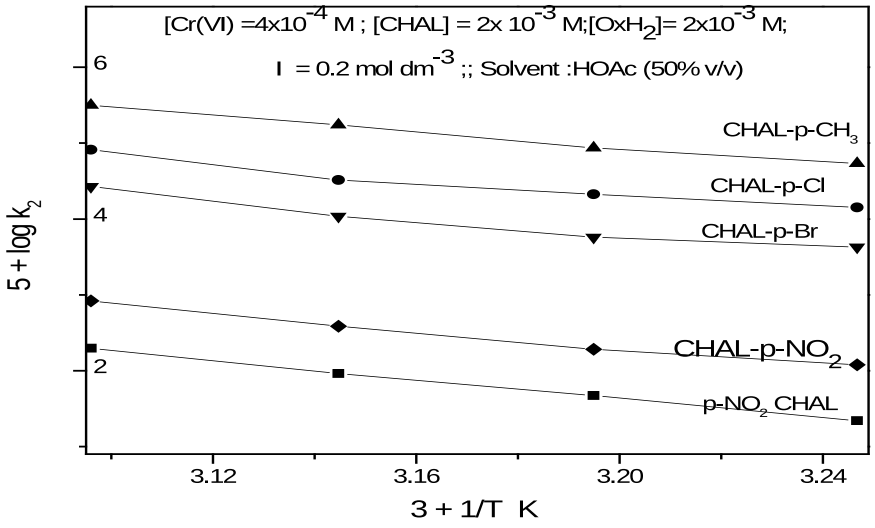


Fig.4: plot of log k_2 versus 1/T

From these plots ,the Arrhenius and activation parameters were evaluated (Table 4)

Table -4: Activation parameters:

[CHAL] = 2.0 x 10^{-3} mol dm^{-3} ; [Cr(VI)] = 4.0 x10^{-4} mol dm^{-3}

[OxH_2] = 2.0 x 10^{-3} mol dm^{-3} ; I = 0.2 mol dm^{-3} ; Temp : 308 K ; Solvent : HOAc (50% v/v)

Substrate	10^4 k_1 (S^{-1})	$\Delta H^{\ddagger}$ kj mol^{-1}	- $\Delta S^{\ddagger}$ J deg -1 mol-^{1}	$\Delta G^{\ddagger}$ kj mol^{-1}
CHAL	0.08245	46.22	165.23	50.77
pCH_3- CHAL	0.12340	44.08	160.50	49.39
pCl- CHAL	0.05435	47.08	164.66	50.67
pBr- CHAL	0.04658	44.66	158.70	48.84
pNO_2-CHAL	0.000218	52.29	180.91	55.67
CHAL-pCH_3	0.53951	43.15	179.33	55.19
CHAL-pCl	0.12022	40.65	166.20	51.15
CHAL-pBr	0.04265	43.98	172.52	53.09
CHAL-pNO_2	0.0011967	46.72	167.94	51.68

The entropy of activation was negative and low, suggesting that the transition state is somewhat (rigid) compared to the reactant the constancy in the values of $\Delta G^{\#}$ for the cooxidation reactions indicating that the same type of mechanism could be operative for the reaction. The isokinetic temperature was computed from Exner plot (figure: 4)

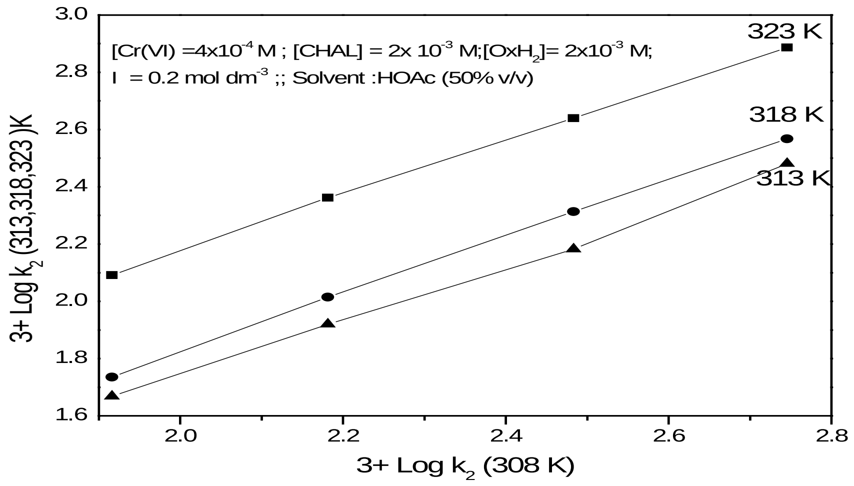
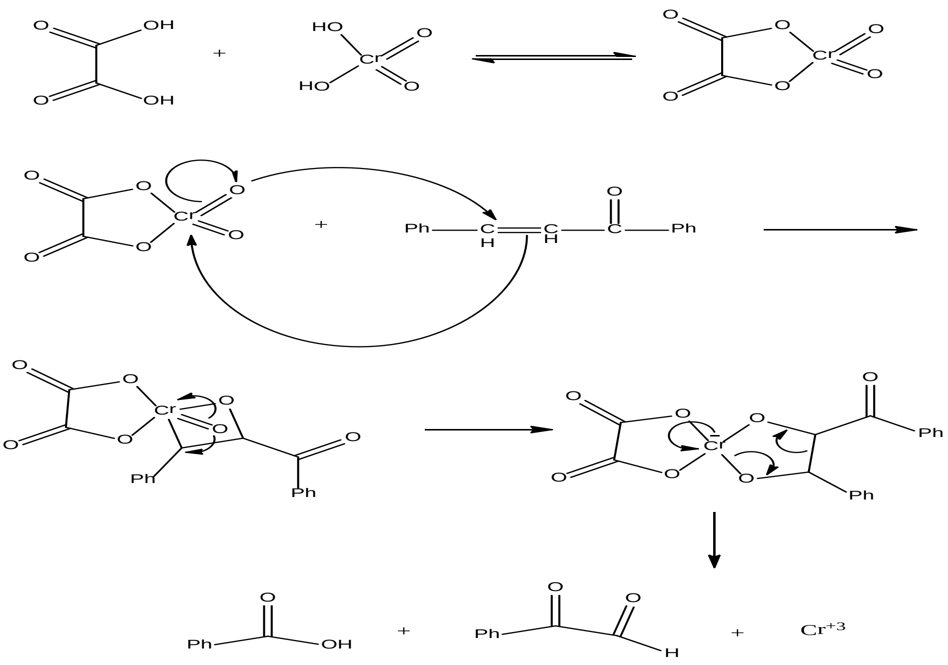


Fig. 4 Exner Plot

4. Mechanism

From the above results obtained of the oxidation of chalcones by Cr(VI) in presence of oxalic acid in aqueous acetic acid medium the proposed mechanism is given as: **Scheme II.**



Scheme II

According to scheme-II, the Chromic acid -oxalic acid complex (C_l) is coordinated to chalcones -acetic acid complex forming a coordinated complex (C_2), in which a hydride shift takes place in a slow step forming a highly unstable entity which then decomposes in a fast step to give the products.

Addition of aluminium nitrate suppresses the oxidation of chalcones with Cr(VI) in the presence of oxalic acid. Chatterjee and coworkers have reported that the chromic acid oxidation of oxalic acid can be effectively prevented by the addition of aluminum nitrate. This effect is probably due to the ability to complex rather firmly with oxalic acid, and thus the formation of the oxalic acid-chromic acid complex, which is an intermediate in the oxidation reaction, is hindered. Rocek and Hasan [28] also report that the rate-accelerating effect of oxalic acid is almost canceled by the addition of aluminum nitrate. These results are in good agreement with the conclusion that the chromic acid-oxalic acid complex is an intermediate in the cooxidation reaction. The unusual high reactivity of the complex composed of a molecule of chromic acid and oxalic acid and a molecule of substrate is explained in this way [28]: that a complex containing both components offers the reaction a more favourable pathway than the oxidation of a single molecule. The presence of the molecule of oxalic acid within the complex facilitates the reduction of Cr(VI) directly to Cr(III), a direct three-electron reduction coupled with the formation of a very stable molecule of carbon dioxide and $^{\bullet}COOH$ species, thus avoiding the formation of the energetically unfavourable Cr(IV) [(28]. The fate of $^{\bullet}CO_2^-$ is explained as

$$^{\bullet}CO_2^- + Cr(VI) \xrightarrow{\text{Fast}} Cr(V) + CO_2$$

$$Cr(VI) + (COOH)_2 \xrightarrow{\text{Fast}} 2CO_2 + Cr(III)$$

Earlier studies lend strong support for this scheme [41].

5. Conclusion

Many of the oxidation reactions which were studied, in presence of the oxalic acid, shown that the rate of oxidation will be increased and the retardation of the rate by electron –withdrawing groups and acceleration of the rate by electron- releasing groups. This study also accounted for the intermediate state which based on the proposed mechanism given .The effect of temperature on the rates of reaction and the thermodynamic parameters were computed . So we conclude that the rate of cooxidation of chalcones in presence of the oxalic acid is higher than that of chalcones alone using chromium (VI).The advantage of this study will help in increasing the knowledge regarding the use of chalcones in the synthesis of medicinal intermediates and in the green chemistry.

Acknowledgement

The authors much thanks to the authorities of King Abdulaziz University for providing supports and facilities.

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